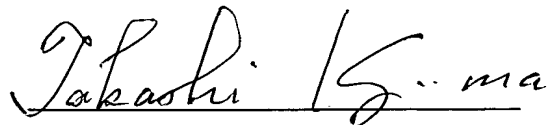




C E R T I F I C A T I O N

I, Takashi KOJIMA of Ginza Ohtsuka Bldg., 2F, 16-12, Ginza 2-chome, Chuo-ku, Tokyo, Japan, hereby certify that I am the translator of the accompanying certified official copy of the documents in respect of an application for a patent filed in Japan on the 7th of March, 2003 and of the official certificate attached thereto, and certify that the following is a true and correct translation to the best of my knowledge and belief.

Dated this 21st day of February, 2005


Takashi KOJIMA



(Translation)

PATENT OFFICE
JAPANESE GOVERNMENT

This is to certify that the annexed is a true copy of the following application as filed with this Office.

Date of Application: March 7, 2003

Application Number: Japanese Patent Application
No. 2003-061476

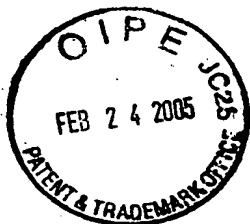
Applicant(s): Shin-Etsu Chemical Co., Ltd.

August 22, 2003

Commissioner,
Patent Office

Yasuo IMAI
(sealed)

Certificate No. 2003-3069006



-1-

2003-061476

[Paper] APPLICATION FOR PATENT

[Reference Number] 15070

[Application Date] March 7, 2003

[Destination] The Commissioner of the Patent Office
Shinichiro OTA

[International Patent Classification]
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[Official Fee]

[Deposit Account Number] 003207

[Amount of Fee] 21000

[List of Documents Attached]

[Document] Specification 1

[Document] Abstract 1

[Necessity of Proof] Yes

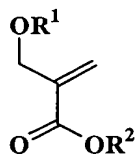
2003-061476

[SPECIFICATION]

[TITLE OF THE INVENTION] Alicyclic Methacrylate Having Oxygen
Substituent Group on α -Methyl

5 [CLAIMS]

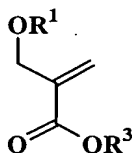
[Claim 1] An alicyclic methacrylate having an oxygen
substituent group on its α -methyl group, represented by the
general formula (1):



(1)

(wherein R¹ is hydrogen or an alkyl group of 1 to 10 carbon
10 atoms which may contain a halogen atom, hydroxyl group,
ether bond, carbonyl group, carboxyl group or cyano group,
and R² is a monovalent organic group of 3 to 20 carbon atoms
having an alicyclic structure.)

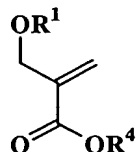
[Claim 2] An alicyclic methacrylate having an oxygen
15 substituent group on its α -methyl group, represented by the
general formula (2):



(2)

(wherein R¹ is hydrogen or an alkyl group of 1 to 10 carbon
atoms which may contain a halogen atom, hydroxyl group,
ether bond, carbonyl group, carboxyl group or cyano group,
20 and R³ is a tertiary alkyl group of 4 to 20 carbon atoms
having an alicyclic structure.)

[Claim 3] An alicyclic methacrylate having an oxygen substituent group on its α -methyl group, represented by the general formula (3):



(3)

(wherein R¹ is hydrogen or an alkyl group of 1 to 10 carbon atoms which may contain a halogen atom, hydroxyl group, ether bond, carbonyl group, carboxyl group or cyano group, and R⁴ is an organic group of 4 to 20 carbon atoms having a lactone structure.)

[DETAILED EXPLANATION OF THE INVENTION]

10 [0001]

[Technical Field of the Invention]

This invention relates to novel alicyclic methacrylate compounds having an oxygen substituent group on their α -methyl group which are useful as monomers for polymerization to form base resins for use in micropatterning resist compositions.

[0002]

[Prior Art]

While a number of recent efforts are being made to achieve a finer pattern rule in the drive for higher integration and operating speeds in LSI devices, deep-ultraviolet lithography is thought to hold particular promise as the next generation in microfabrication technology. In particular, photolithography using a KrF or ArF excimer laser as the light source is strongly desired to reach the practical level as the micropatterning technique capable of achieving a feature size of 0.3 μm or less.

[0003]

The resist materials for use in photolithography using light of an excimer laser, especially ArF excimer laser having a wavelength of 193 nm, are, of course, required to have a high transparency to light of that wavelength. In addition, they are required to have an etching resistance sufficient to allow for film thickness reduction, a high sensitivity sufficient to eliminate any extra burden on the expensive optical material, and especially, a high resolution sufficient to form a precise micropattern. To meet these requirements, it is crucial to develop a base resin having a high transparency, rigidity and reactivity. None of the currently available polymers satisfy all of these requirements. There exists a strong demand to further improve resist materials.

[0004]

Most common among high transparency resins used in the art are copolymers of acrylic or methacrylic acid derivatives. Active research works have been made on these copolymers to use them effectively as resist material. Patent Document 1: JP-A 4-39665 describes that an alicyclic structure such as adamantyl must be introduced as an ester substituent group into copolymers of acrylic or methacrylic acid derivatives in order to enhance the structural rigidity of the backbone and to provide necessary etching resistance. The introduction of an alicyclic structure, on the other hand, increases the water repellency of polymers, which disturbs smooth development with an aqueous tetramethylammonium hydroxide solution, a developer, tending to have deleterious effects of forming micro-patterns with configuration defects and eventually incurring pattern disruption. When these polymers are formulated as the base resin into resist compositions, the resulting resist compositions in some cases have satisfactory resolution, but do not withstand etching, and in other cases, have acceptable etch resistance, but a low resolution and insufficient performance.

[0005]

[Patent Document 1]

JP-A 4-39665

[0006]

5 [Problem to be Solved by the Invention]

The present invention has been done in view of the above circumstances. An object of the invention is to provide an alicyclic methacrylate compound having an oxygen substituent group on its α -methyl group which is useful as a monomer for polymerization to form a base resin for use in a micropatterning resist composition which is improved in both etching resistance and resolution when processed by photolithography using light with a wavelength of up to 300 nm, especially ArF excimer laser light as the light source.

15 [0007]

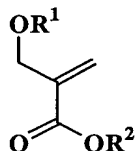
[Means for Solving the Problem and Embodiment of the Invention]

The present inventors have earnestly studied in order to attain the above object. As a result, it has been found that alicyclic methacrylate compounds having an oxygen substituent group on their α -methyl group, represented by the general formulae (1), (2) and (3) below, are readily synthesized by the method described later in high yields, that polymers obtained through polymerization of these alicyclic methacrylate compounds having an oxygen substituent group on their α -methyl group have high transparency at the exposure wavelength of an excimer laser, and that resist compositions using the polymers as the base resin have improved etching resistance and resolution upon lithographic processing. It is believed that the alicyclic moiety in the inventive compounds largely contributes to the enhancement of etching resistance. With respect to the improvement in resolution, it is believed that the presence of an oxymethyl group in the inventive compounds increases the hydrophilicity in proximity to the polymer backbone, enabling more smooth development.

[0008]

The invention provides the following alicyclic methacrylate having an oxygen substituent group on its α -methyl group.

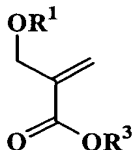
- 5 [1] An alicyclic methacrylate having an oxygen substituent group on its α -methyl group, represented by the general formula (1):



(1)

- (wherein R¹ is hydrogen or an alkyl group of 1 to 10 carbon atoms which may contain a halogen atom, hydroxyl group, ether bond, carbonyl group, carboxyl group or cyano group, and R² is a monovalent organic group of 3 to 20 carbon atoms having an alicyclic structure.)

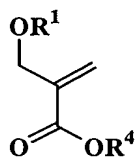
- 10 [II] An alicyclic methacrylate having an oxygen substituent group on its α -methyl group, represented by the general formula (2):



(2)

- (wherein R¹ is hydrogen or an alkyl group of 1 to 10 carbon atoms which may contain a halogen atom, hydroxyl group, ether bond, carbonyl group, carboxyl group or cyano group, and R³ is a tertiary alkyl group of 4 to 20 carbon atoms having an alicyclic structure.)

- 20 [III] An alicyclic methacrylate having an oxygen substituent group on its α -methyl group, represented by the general formula (3):



(3)

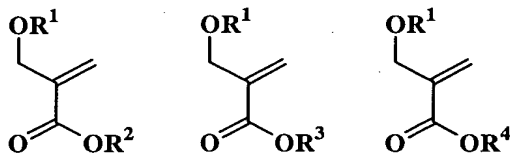
(wherein R¹ is hydrogen or an alkyl group of 1 to 10 carbon atoms which may contain a halogen atom, hydroxyl group, ether bond, carbonyl group, carboxyl group or cyano group, and R⁴ is an organic group of 4 to 20 carbon atoms having a
5 lactone structure.)

[0009]

The following is the detailed description of the invention.

The alicyclic methacrylate compounds having an oxygen
10 substituent group on their α-methyl group of the present invention have the general formulae (1), (2) and (3).

[0010]



(1)

(2)

(3)

(In the formulae, R¹ is hydrogen or an alkyl group of 1 to 10 carbon atoms which may contain a halogen atom, hydroxyl
15 group, ether bond, carbonyl group, carboxyl group or cyano group. R² is a monovalent organic group of 3 to 20 carbon atoms having an alicyclic structure. R³ is a tertiary alkyl group of 4 to 20 carbon atoms having an alicyclic structure. R⁴ is an organic group of 4 to 20 carbon atoms having a
20 lactone structure.)

[0011]

The C₁-C₁₀ alkyl group represented by R¹ may be either straight, branched or cyclic and contain a halogen atom,

hydroxyl group, ether bond, carbonyl group, carboxyl group or cyano group. Suitable alkyl groups are illustrated by methyl, ethyl, propyl, 2-propyl, butyl, 2-butyl, isobutyl, t-butyl, pentyl, hexyl, cyclohexyl, decyl, chloromethyl, dichloromethyl, trichloromethyl, trifluoromethyl, 2-hydroxyethyl, 2-hydroxypropyl, methoxymethyl, ethoxymethyl, 2-methoxyethoxymethyl, 1-ethoxyethyl, 2-tetrahydropyranyl, formyl, acetyl, methoxyacetyl, acetoxyacetyl, cyanomethyl, and 2-cyanoethyl.

10 [0012]

Examples of the monovalent C_3 - C_{20} organic group having an alicyclic structure represented by R^2 include cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, dicycloheptyl, dicyclooctyl, dicyclononyl, dicyclodecanyl, tricyclodecanyl, adamantyl, tetracyclododecanyl, cyclohexylmethyl, dicycloheptylmethyl, isobornyl, menthyl, hydroxycyclohexyl, hydroxydicycloheptyl, and hydroxyadamantyl as well as those groups illustrated for R^3 and R^4 later.

20 [0013]

Examples of the C_4 - C_{20} tertiary alkyl group having an alicyclic structure represented by R^3 include

1-methylcyclopropyl, 1-methylcyclopentyl, 1-ethylcyclopentyl, 1-methylcyclohexyl, 1-ethylcyclohexyl, 1-cyclopentylcyclopentyl, 1-cyclohexylcyclopentyl, 1-cyclopentylcyclohexyl, 1-cyclohexylcyclohexyl, 2-methyl-2-norbornyl, 2-ethyl-2-norbornyl, 8-methyl-8-tricyclo[5.2.1.0^{2,6}]decyl, 8-ethyl-8-tricyclo[5.2.1.0^{2,6}]decyl, 3-methyl-3-tetracyclo[4.4.0.1^{2,5},1^{7,10}]dodecyl, 3-ethyl-3-tetracyclo[4.4.0.1^{2,5},1^{7,10}]dodecyl, 2-methyl-2-adamantyl, 2-ethyl-2-adamantyl, 1-adamantyl-1-methylethyl, 1-methyl-3-oxo-1-cyclohexyl, 1-methyl-1-(tetrahydrofuran-2-yl)ethyl, 5-hydroxy-2-methyl-2-adamantyl, and 5-hydroxy-2-ethyl-2-adamantyl.

[0014]

Examples of the C₄-C₂₀ organic group having a lactone structure represented by R⁴ include butyrolactonyl, valerolactonyl, 1,3-cyclohexanecarbolactonyl,

5 4-oxa-5-oxotricyclo[5.2.1.0^{2,6}]decyl,
2,6-norbornanecarbolacton-3-ylmethyl,
2,6-norbornanecarbolacton-5-yl,
3-methoxycarbonyl-2,6-norbornanecarbolacton-5-yl, and
7-oxa-2,6-norbornanecarbolacton-5-yl.

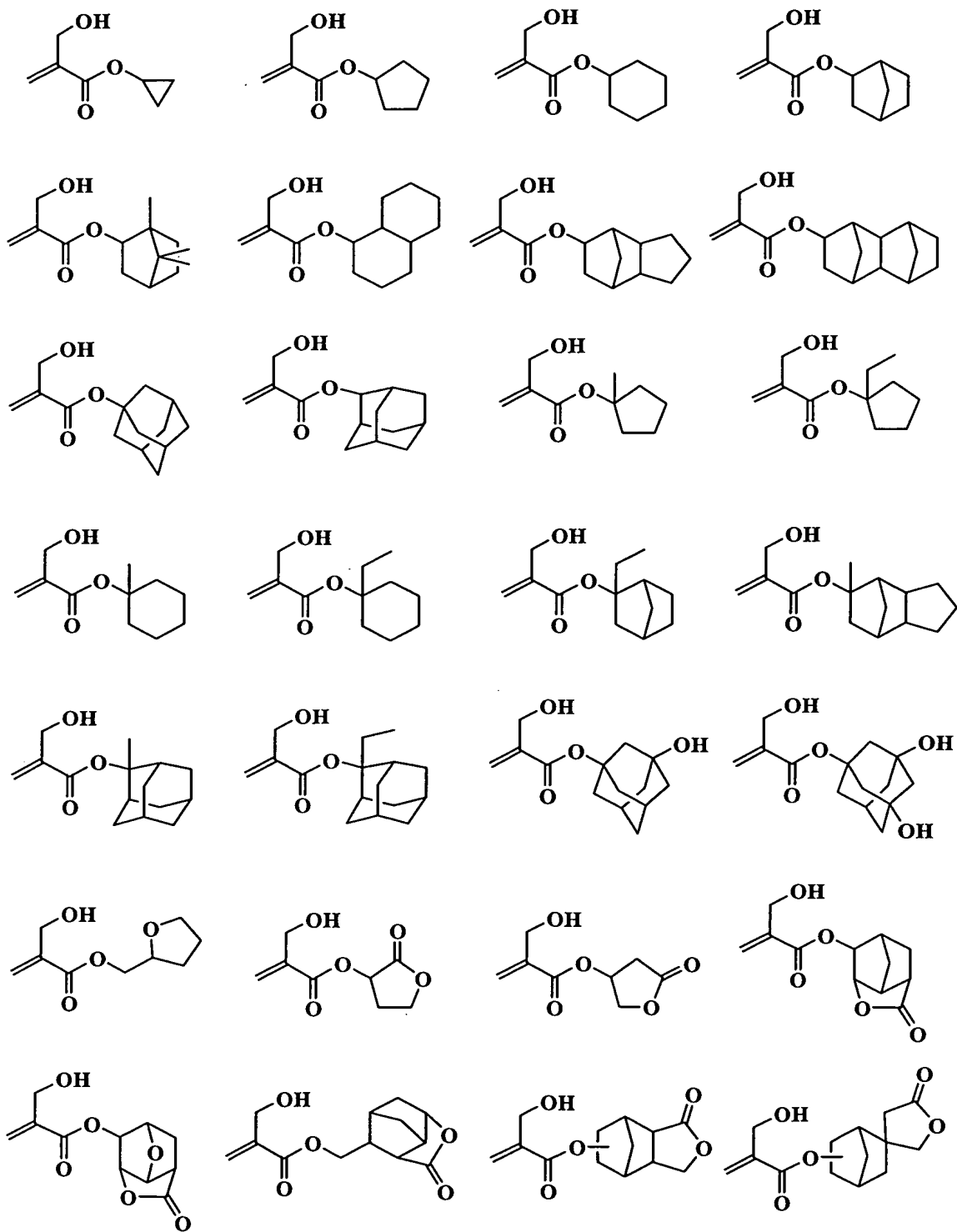
10 [0015]

By properly choosing R¹ and R², R³ or R⁴ in accordance with a particular application, it is possible to optimize the polarity and other properties of an overall molecule and eventually, the characteristics of a photoresist utilizing
15 the inventive compound.

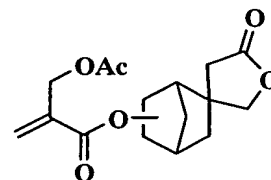
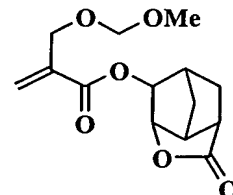
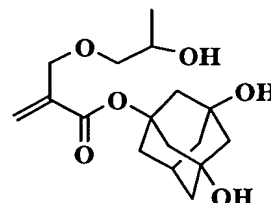
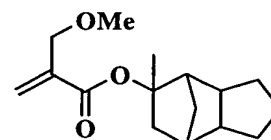
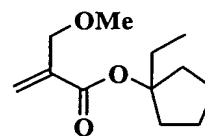
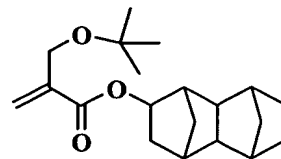
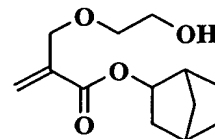
[0016]

Illustrative, non-limiting, examples of the ester compounds of the invention are given below. In the following formulae, Me is methyl, Ac is acetyl and Et is
20 ethyl.

[0017]



[0018]



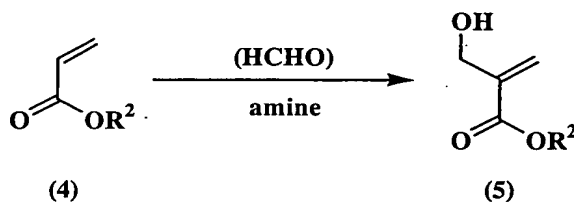
[0019]

The alicyclic methacrylate compound having an oxygen substituent group on the α -methyl group, represented by the formula (1), according to the present invention can be prepared, for example, by the synthesis process described below. In the practice of the invention, the synthesis process is not limited thereto. The following is the detailed description.

[0020]

Reference is first made to the compound of formula (1) wherein $R^1 = H$. It can be synthesized, as shown by the reaction scheme below, in one step from a corresponding acrylate compound of formula (4) which has been prepared by a routine process. This reaction is a hydroxymethylation of the acrylate compound at the α -position as shown below. One molar equivalent of a formaldehyde equivalent reacts on the acrylate compound of formula (4) in a solvent or solventless system in the presence of an amine compound to form an α -(hydroxymethyl)acrylate compound of formula (5).

[0021]



(In the formulae, R^2 is a monovalent C_3 - C_{20} organic group having an alicyclic structure.)

[0022]

The amine compound used in the hydroxymethylation is illustrated by trimethylamine, triethylamine, tributylamine, pyridine, 4-dimethylaminopyridine, 1,4-diazabicyclo[2.2.2]octane, 1,5-diazabicyclo[4.3.0]non-5-ene, and 1,8-diazabicyclo[5.4.0]undec-7-ene. An appropriate amount of the amine compound used is 0.001 to 10 moles, especially 0.01 to 1 mole per mole of the starting reactant. With less than 0.001 mole of the amine, the reaction may not

proceed. More than 10 moles of the amine is wasteful because no further effect corresponding to such an excess may be exerted.

[0023]

5 The formaldehyde equivalent is illustrated by gaseous formaldehyde, formalin, paraformaldehyde and 1,3,5-trioxane. An appropriate amount of the formaldehyde equivalent used is 0.2 to 10 moles, especially 0.5 to 2 moles of formaldehyde per mole of the starting reactant. With less than 0.2 mole
10 of formaldehyde, a large portion of the starting reactant, acrylate compound may be left, leading to very low yields. More than 10 moles of formaldehyde can form a large amount of by-product, also leading to very low yields.

[0024]

15 Examples of the solvent, if used in the hydroxymethylation, include hydrocarbons such as toluene, hexane and heptane; ethers such as dibutyl ether, diethylene glycol diethyl ether and tetrahydrofuran; alcohols such as methanol and ethanol; halogenated hydrocarbons such as
20 methylene chloride; esters such as ethyl acetate; ketones such as acetone and 2-butanone; nitriles such as acetonitrile; and aprotic polar solvents such as dimethyl sulfoxide, N,N-dimethylformamide and N,N-dimethylacetamide; and water. These solvents may be used alone or in admixture
25 of any.

[0025]

 The temperature for the hydroxymethylation is preferably in the range of -20°C to 100°C. An appropriate reaction temperature may be selected in the range depending
30 on the reactants and reaction conditions. In an instance where reaction is effected in water using 1,4-diazabicyclo[2.2.2]octane as the amine compound and formaldehyde as the formaldehyde equivalent, a temperature in the range of 0°C to 60°C is preferred. As the reaction
35 temperature raises, more side reactions occur and more formaldehyde is evaporated off. It is thus important for achieving high yields to perform the reaction at a

permissible lower temperature within the range where the reaction proceeds at a practically acceptable rate.

[0026]

For increased yields, the reaction time of the addition reaction is desirably determined by monitoring the progress of reaction by thin-layer chromatography, gas chromatography or the like. The reaction time is usually about 1 to about 200 hours.

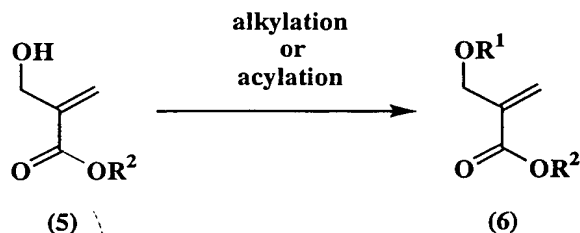
[0027]

At the end of reaction, the target compound (5), α -(hydroxymethyl)acrylate compound is recovered by a conventional aqueous workup. The target compound (5) can be purified by any conventional technique such as recrystallization, chromatography or distillation.

[0028]

Next reference is made to the compound of formula (1) wherein R^1 is a C_1 - C_{10} alkyl group which may contain a halogen atom, hydroxyl group, ether bond, carbonyl group, carboxyl group or cyano group. By subjecting the above-obtained α -(hydroxymethyl)acrylate compound of formula (5) to alkylation or acylation in a conventional way, as shown by the reaction scheme below, an target compound of formula (6) can be synthesized. The resulting α -(alkoxymethyl) or α -(acyloxymethyl)acrylate compound of formula (6) can be purified by any conventional technique such as recrystallization, chromatography or distillation.

[0029]



(In the formulae, R^1 is a C_1 - C_{10} alkyl group which may contain a halogen atom, hydroxyl group, ether bond, carbonyl group, carboxyl group or cyano group; and R^2 is a monovalent C_3 - C_{20} organic group having an alicyclic structure.)

5 [0030]

The inventive compounds are useful as monomers to form polymers which serve effectively as the base resin in photoresist compositions.

[0031]

10 Preparation of a polymer using the inventive alicyclic methacrylate compound having an oxygen substituent group on their α -methyl group as a monomer is generally carried out by mixing the monomer with a solvent, adding a catalyst or polymerization initiator thereto, and effecting
15 polymerization reaction while heating or cooling if necessary. This polymerization may be done by any conventional technique such as radical, cationic and anionic polymerization techniques. One or more other compounds having a polymerizable double bond can be copolymerized if
20 necessary.

[0032]

The polymer resulting from the above-described polymerization is used as a base resin to formulate a resist composition. The resist composition is generally formulated
25 by adding an organic solvent and a photoacid generator to the base resin. If necessary, a crosslinking agent, a basic compound, a dissolution inhibitor and the like are further added. Preparation of resist compositions may be done in a conventional way.

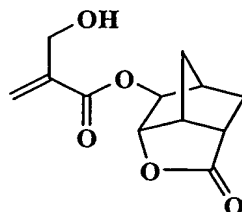
30 [0033]

[EXAMPLE]

Examples and Reference Examples of the invention are given below by way of illustration and not by way of limitation. In the formulae below, Me is methyl and Ac is
35 acetyl.

[0034]

[Example 1] Synthesis of 2,6-norbornanecarbolacton-5-yl
 α -(hydroxymethyl)acrylate



(7)

[0035]

5 118 g of 2,6-norbornanecarbolacton-5-yl acrylate, 31.8
g of 1,4-diazabicyclo[2.2.2]octane, 50.6 g of 37% formalin
and 250 g of tetrahydrofuran were combined and stirred for
20 hours. The reaction solution was neutralized with
hydrochloric acid, followed by conventional aqueous workup.
10 The solvent was distilled off in vacuo, after which the
product was purified by silica gel chromatography, obtaining
81.0 g (yield 60%) of 2,6-norbornanecarbolacton-5-yl
 α -(hydroxymethyl)acrylate represented by formula (7).

(Results of IR and NMR analyses)

15 IR (thin film):

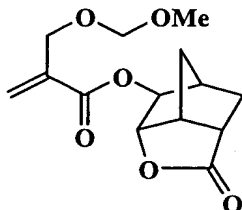
ν = 3479, 2980, 2883, 1782, 1716, 1637, 1452, 1396,
1342, 1308, 1267, 1180, 1163, 1151, 1057, 1043, 1028,
1012, 998, 954 cm^{-1}

$^1\text{H-NMR}$ (600 MHz in CDCl_3):

20 δ = 1.58 (1H, br. d, J = 11.6 Hz), 1.69 (1H, br. d, J =
13.8 Hz), 1.93 (1H, br. d, J = 11.6 Hz), 1.97 (1H, ddd,
 J = 13.7, 11.3, 4.5 Hz), 2.24 (1H, br. s), 2.46-2.52
(2H, m), 3.14 (1H, m), 4.23 (2H, s), 4.49 (1H, d, J =
4.8 Hz), 4.58 (1H, m), 5.81 (1H, d, J = 1.0 Hz), 6.15
25 (1H, d, J = 1.0 Hz)

[0036]

[Example 2] Synthesis of 2,6-norbornanecarbolacton-5-yl
 α -(methoxymethoxymethyl)acrylate



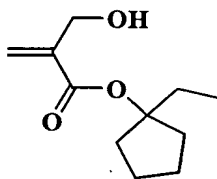
(8)

[0037]

5 With stirring, 9.7 g of chloromethyl methyl ether was added to a mixture of 23.8 g of 2,6-norbornanecarbolacton-5-yl α -(hydroxymethyl)acrylate obtained in Example 1, 15.2 g of triethylamine and 200 g of acetonitrile. After 20 hours of stirring, water was added to the reaction solution to stop
10 the reaction. This was followed by conventional aqueous workup. The solvent was distilled off in vacuo, after which the product was purified by silica gel chromatography, obtaining 22.0 g (yield 78%) of 2,6-norbornanecarbolacton-5-yl α -(methoxymethoxymethyl)acrylate represented by formula
15 (8).

[0038]

[Example 3] Synthesis of 1-ethylcyclopentyl
 α -(hydroxymethyl)acrylate



(9)

20 [0039]

Reaction was performed as in Example 1 except that 95.4 g of 1-ethylcyclopentyl acrylate was used instead of 2,6-norbornanecarbolacton-5-yl acrylate. Purification by vacuum distillation (boiling point 82°C/30 Pa) gave

1-ethylcyclopentyl α -(hydroxymethyl)acrylate represented by formula (9). The yield was 68%.

(Results of IR and NMR analyses)

IR (thin film):

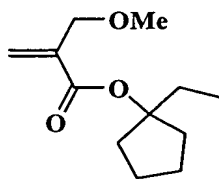
5 $\nu = 3466, 2970, 2877, 1707, 1635, 1462, 1392, 1336,$
1273, 1227, 1163, 1113, 1055, 949 cm^{-1}

^1H -NMR (600 MHz in CDCl_3):

$\delta = 0.86$ (3H, m), 1.56-1.76 (6H, m), 2.01 (2H, m), 2.14
10 (2H, m), 2.61 (1H, br), 4.28 (2H, s), 5.74 (1H, m),
6.16 (1H, m)

[0040]

[Example 4] Synthesis of 1-ethylcyclopentyl
 α -(methoxymethyl)acrylate



(10)

15

[0041]

A mixture of 19.8 g of 1-ethylcyclopentyl
 α -(hydroxymethyl)acrylate, 40.0 g of methyl iodide, 30.0 g
of silver (I) oxide and 50 g of N,N-dimethylformamide was
20 stirred at 50°C for 30 hours. The solids were filtered off,
followed by conventional aqueous workup. The solvent was
distilled off in vacuo. Purification by distillation
(boiling point 53°C/16 Pa) gave 1-ethylcyclopentyl
 α -(methoxymethyl)acrylate represented by formula (10). The
25 yield was 62%.

(Results of IR and NMR analyses)

IR (thin film):

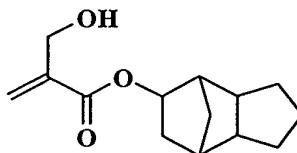
$\nu = 2970, 1939, 2877, 2835, 2816, 1720, 1709, 1637,$
1460, 1396, 1323, 1277, 1161, 1113, 948 cm^{-1}

¹H-NMR (600 MHz in CDCl₃):

δ = 0.86 (3H, t, J = 7.6 Hz), 1.58-1.75 (6H, m), 2.00 (2H, q, J = 7.6 Hz), 2.14 (2H, m), 3.38 (3H, s), 4.09 (2H, dd), 5.76 (1H, dt), 6.20 (1H, dt)

5 [0042]

[Example 5] Synthesis of 8-tricyclo[5.2.1.0^{2,6}]decyl
α-(hydroxymethyl)acrylate



(11)

[0043]

The procedure of Example 1 was repeated except that
10 117 g of 8-tricyclo[5.2.1.0^{2,6}]decyl acrylate was used instead
of 2,6-norbornanecarbolacton-5-yl acrylate. There was
obtained 8-tricyclo[5.2.1.0^{2,6}]decyl α-(hydroxymethyl)acrylate
represented by formula (11). The yield was 60%.
(Results of IR and NMR analyses)

15 IR (thin film):

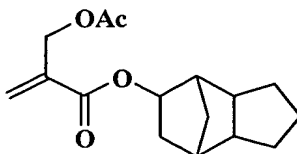
ν = 3467, 2949, 2862, 1709, 1635, 1475, 1448, 1396,
1309, 1267, 1223, 1157, 1134, 1055, 1022, 984, 947 cm⁻¹

¹H-NMR (600 MHz in CDCl₃):

20 δ = 0.88-1.00 (2H, m), 1.22 (1H, dtt, J = 12.4, 12.4,
6.9 Hz), 1.29 (1H, m), 1.36 (1H, m), 1.45 (1H, ddd, J =
13.4, 4.5, 2.1 Hz), 1.63-1.72 (2H, m), 1.73-1.90 (4H,
m), 2.04 (1H, d, J = 4.5 Hz), 2.11 (1H, s), 2.40 (1H,
br. s), 4.30 (2H, s), 4.65 (1H, J = 7.2 Hz), 5.78 (1H,
m), 6.19 (1H, d, J = 1.0 Hz)

[0044]

[Example 6] Synthesis of 8-tricyclo[5.2.1.0^{2,6}]decyl
α-(acetoxymethyl)acrylate



(12)

[0045]

5 To a mixture of 23.6 g of 8-tricyclo[5.2.1.0^{2,6}]decyl
α-(hydroxymethyl)acrylate and 15.8 g of pyridine was added
15.3 g of acetic anhydride. The mixture was stirred for 20
hours. Water was added to the reaction solution to stop the
reaction, followed by conventional aqueous workup. The
10 solvent was distilled off in vacuo. Purification by
distillation (boiling point 123°C/13 Pa) gave 23.7 g (yield
90%) of 8-tricyclo[5.2.1.0^{2,6}]decyl α-(acetoxymethyl)acrylate
represented by formula (12).

(Results of IR and NMR analyses)

15 IR (thin film):

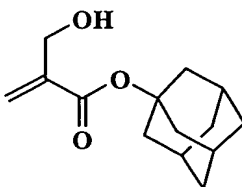
$\nu = 2951, 2864, 1749, 1722, 1643, 1475, 1448, 1400,$
 $1369, 1311, 1271, 1228, 1184, 1167, 1157, 1134, 1047,$
 $982, 953 \text{ cm}^{-1}$

¹H-NMR (600 MHz in CDCl₃):

20 $\delta = 0.88\text{-}0.99$ (2H, m), 1.21 (1H, dtt, $J = 12.4, 12.4,$
6.5 Hz), 1.28 (1H, dt, $J = 10.3, 1.2$ Hz), 1.35 (1H, br.
d, $J = 10.3$ Hz), 1.44 (1H, ddd, $J = 13.4, 4.5, 2.1$ Hz),
1.62-1.70 (2H, m), 1.72-1.89 (4H, m), 2.03 (1H, d, $J =$
4.5 Hz), 2.08 (3H, s), 2.11 (1H, br. s), 4.65 (1H, br.
25 d, $J = 6.9$ Hz), 4.77 (2H, br. s), 5.78 (1H, m), 6.31
(1H, d, $J = 1.0$ Hz)

[0046]

[Example 7] Synthesis of 1-adamantyl
 α -(hydroxymethyl)acrylate



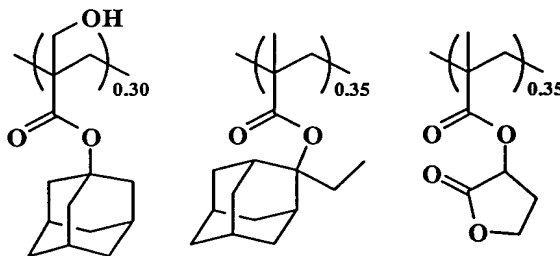
(13)

5 [0047]

The procedure of Example 1 was repeated except that 117 g of 1-adamantyl acrylate was used instead of 2,6-norbornanecarbolacton-5-yl acrylate. There was obtained 1-adamantyl α -(hydroxymethyl)acrylate represented by formula
10 (13) (yield 60%).

[0048]

[Reference Example 1] Synthesis of a polymer using inventive α -(oxymethyl)acrylic acid ester



(14)

[0049]

15 In a nitrogen atmosphere, a mixture of 7.1 g of 1-adamantyl α -(hydroxymethyl)acrylate obtained in Example 7, 8.7 g of 2-ethyl-2-adamantyl methacrylate, 6.0 g of 2-oxotetrahydrofuran-3-yl methacrylate, 60 mg of N,N'-azobisisobutyronitrile, and 80 ml of tetrahydrofuran
20 was heated and stirred at 60°C for 20 hours. After cooling, the reaction mixture was added dropwise to 2 liters of methanol under vigorous stirring. The precipitate which settled down was collected by filtration. The solids were

washed with methanol and dried in vacuo, obtaining 16.4 g of the target polymer of formula (14). The yield was 75%. An component ratio calculated from its ¹H-NMR spectrum indicated a copolymerization ratio of approximately 30:35:35. GPC analysis using polystyrene standards indicated a weight average molecular weight (Mw) of 9,800 and a polydispersity index (Mw/Mn) of 1.80.

[0050]

[Reference Example 2] Resist pattern formation using polymer

Using the polymer obtained in Reference Example 1, a resist material was prepared. Its composition was:
(A) 80 parts by weight of the polymer of Reference Example 1 as a base polymer,
(B) 1.0 part by weight of triphenylsulfonium trifluoromethanesulfonate as a photoacid generator,
(C) 480 parts by weight of propylene glycol monomethyl ether acetate as a solvent, and
(D) 0.08 part by weight of tributylamine as a basic compound.

This was passed through a Teflon® filter having a pore diameter of 0.2 μm. The resist solution was spin coated on a silicon wafer having hexamethyldisilazane sprayed thereon at 90°C for 40 seconds and heat treated at 120°C for 90 seconds, forming a resist film of 500 nm thick. The resist film was exposed to ArF excimer laser light, heat treated at 120°C for 90 seconds, cooled down to 23°C, and dipped in a 2.38% tetramethylammonium hydroxide aqueous solution at 23°C for 60 seconds for development, thereby forming a 1:1 line-and-space pattern. The wafer as developed was observed under top-down SEM. Patterns down to a line width of 0.13 μm existed without collapse or stripping and hence, resolved. This demonstrates that the photoresist material of the invention has improved resolution.

[0051]

[Reference Example 3] Transparency of polymer

The polymer obtained in Reference Example 1, 1.0 g, was dissolved in 6.0 g of cyclohexanone, which was passed

through a Teflon® filter having a pore diameter of 0.2 μm . The solution was spin coated on a quartz substrate and heat treated at 90°C for 60 seconds, forming a thin film of 500 nm thick. The thin film was measured for transmittance at 193 nm using a UV-visible spectrophotometer, finding a transmittance of 76% per 500 nm of film thickness. This result demonstrates that the polymer according to the invention has a sufficient transparency as the photoresist base polymer for excimer laser photolithography.

10 [0052]

[Reference Example 4] Etching resistance of polymer

The polymer obtained in Reference Example 1, 2 g, was dissolved in 10 g of cyclohexanone, which was passed through a Teflon® filter having a pore diameter of 0.2 μm . The solution was spin coated on a silicon wafer and heat treated at 90°C for 60 seconds, forming a thin film of 700 nm thick. Using a reactive ion etching apparatus, the thin film was etched with CF_4 gas under conditions: power 100 W, pressure 5 Pa, and gas flow rate 30 ml/min. As a result, the etching rate was 1.10 based on a rate of 1.00 normalized for novolac resist. For comparison purposes, the same test was done on poly(p-hydroxystyrene) used as the base polymer for KrF resist, finding an etching rate of 1.20. These results demonstrate that the polymer according to the invention has a slower etching rate with CF_4 gas, that is, better dry etching resistance.

[0053]

[Effect of the Invention]

The polymers prepared from the inventive alicyclic methacrylate compounds having an oxygen substituent group on their α -methyl group have improved transparency, especially at the exposure wavelength of an excimer laser, and improved dry etching resistance. Resist compositions comprising polymers prepared from the inventive alicyclic methacrylate compounds having an oxygen substituent group on their α -methyl group are sensitive to high-energy radiation, show

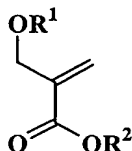
a high resolution, allow smooth development and thus lend themselves to micropatterning. The resist compositions are thus suitable as micropatterning material for VLSI fabrication. Accordingly, the inventive alicyclic
5 methacrylate compounds having an oxygen substituent group on their α -methyl group are quite useful as monomers to form base polymers for resist compositions in satisfying both the resolution and etching resistance of resist.

2003-061476

[ABSTRACT]

[Means for Solution]

An alicyclic methacrylate having an oxygen substituent group
5 on its α -methyl group, represented by the formula (1):



(1)

(R¹ is hydrogen or an alkyl group of 1 to 10 carbon atoms which
may contain a halogen atom, hydroxyl group, ether bond, carbonyl
group, carboxyl group or cyano group, and R² is a monovalent organic
group of 3 to 20 carbon atoms having an alicyclic structure.)

10 [Effect]

The polymers prepared from the inventive alicyclic
methacrylate compounds having an oxygen substituent group on their
 α -methyl group have improved transparency, especially at the
exposure wavelength of an excimer laser, and improved dry etching
15 resistance. Resist compositions comprising polymers prepared
from the inventive compounds are sensitive to high-energy radiation,
show a high resolution, allow smooth development and thus lend
themselves to micropatterning. The resist compositions are thus
suitable as micropatterning material for VLSI fabrication.

20 [Selected Drawing] none